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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/CA97/00122 (22) International Filing Date: 21 February 1997 (21.02.97) (30) Priority Data: 9603741.1 22 February 1996 (22.02.96) GB (71) Applicant (for all designated States except US): ENPAR TECHNOLOGIES INC. [CA/CA]; 151 Dovercliffe Road, Guelph, Ontario N1G 3A5 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): LIN, Mei [CN/CA]; 151 Dovercliffe Road, Guelph, Ontario N1G 3A5 (CA). SHELPI, Gene, Sidney [CA/CA]; 151 Dovercliffe Road, Guelph, Ontario N1G 3A5 (CA). CHESWORTH, Ward [CA/CA]; 131 York Street, Eden Mills, Ontario N0B 1P0 (CA). (74) Agent: ASQUITH, Anthony; 173 Westvale Drive, Waterloo, Ontario N2T 1B7 (CA).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: ELECTROCHEMICAL TREATMENT OF WATER CONTAMINATED WITH NITROGENOUS COMPOUNDS (57) Abstract Waters contaminated by nitrogenous compounds such as nitrate, ammonium, etc., are treated by electrochemical transformation of the contaminant to nitrogen gas. Electrodes are placed in the contaminated water to form a cell, in which the voltage of one of the electrodes is set to the Eh voltage at which nitrogen gas is thermodynamically favoured. The cell may be electrolytic or galvanic.		

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1 Title: ELECTROCHEMICAL TREATMENT OF WATER CONTAMINATED WITH
2 NITROGENOUS COMPOUNDS

3
4 This invention relates to the treatment of polluted or contaminated water by
5 electrochemical treatment (which includes both galvanic and electrolytic treatment).
6 The invention is intended to be applied to waters contaminated by dissolved
7 nitrogenous compounds.

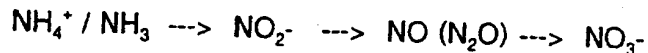
8
9 In conventional cases where electrolysis has been used for treating contaminated
10 water, the reactions that have been utilised have been those, for example, which take
11 metals out of solution by cathode deposition.

12
13 Work has been done on the use of electrolysis for treating effluent from manufacturing
14 establishments, where the water is polluted with a specific pollutant. But those
15 systems were special in that the effluent water was already contained, and the
16 research effort was directed to cleaning up or recovering specific contaminants, at
17 known concentrations, and in a system that was designed to cater for the pollutant
18 when the factory was built.

19
20 Ammonium (NH_4^+) in sewage water can be broken down by bacterial action. Much
21 consideration and effort has been applied over many years to engineering the
22 ammonium breakdown reaction on a large scale, in the context of municipal sewage
23 water treatment. Generally, bacteria promote oxidation of the ammonium into nitrate;
24 other bacteria then promote denitrification or reduction of the nitrate to nitrogen gas.
25 The reaction has been engineered by providing an environment in which bacteria can
26 effect the oxidation and reduction.

27
28 Some shortcomings of this conventional procedure will now be discussed. The
29 biological oxidation of ammonium to nitrate and the subsequent reduction of the
30 nitrate to nitrogen gas, has undesirable side-effects. Other compounds of nitrogen
31 are formed, such as nitric oxide (NO), nitrous oxide (N_2O), and nitrogen dioxide (NO_2),
32 which are considered to be either directly toxic to humans and other animals, or
33 harmful to the ozone layer or other aspects of the environment.

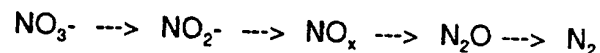
One problem is that the conversion of ammonium to nitrogen, via nitrate, done microbiologically, as in the conventional systems, has been far from complete. Significant quantities of the nitrogen oxides can be released, as gases, during the reactions, in addition to the nitrogen gas. When, as in the conventional systems, the oxidation of ammonium /ammonia occurred biologically (nitrification), the reaction pathway may be described as:



whereby the harmful intermediate gaseous compounds may escape into the atmosphere.

Also, the nitrate produced by the ammonium breakdown cannot be left in the water. And nitrate itself, for example from agricultural run-off, may be present as a nitrogenous contaminant per se, in groundwater.

When the reduction of nitrate occurred biologically (denitrification), the reaction pathway may be described as:



Again, the intermediate gaseous compounds may escape.

Another point that should be noted is that the efficiency of the conventional biochemical nitrification and denitrification reactions is affected by cold weather, whereby it is found that the gases released to the atmosphere in the winter contain an even larger proportion of N_2O and NO_x gases. This is a marked disadvantage of the conventional systems. In some cases, also, the temperature can be so low that biological reactions substantially do not take place at all, and breakdown of the contaminants has to await warmer weather.

It is recognised that the electrochemical reactions as described herein have the potential to proceed at lower temperatures than the conventional biological processes. They may therefore be suitable for cold-climate applications, where biological remediation is ineffective for most of the year.

GENERAL FEATURES OF THE INVENTION

1 It is recognised in the invention that, in order to remove nitrogenous contamination,
2 the nitrogenous contaminants can be transformed, by engineered electrochemical
3 processes, directly into nitrogen gas. (Nitrogen gas of course already comprises 4/5
4 of the atmosphere, and its release is not harmful.)

5
6 It is also recognised that inorganic electrochemical reactions can be used to drive
7 both kinds of breakdown reaction, i.e the oxidation of e.g ammonium, and the
8 reduction of e.g nitrate, both to gaseous nitrogen directly, whereby the production and
9 release of the harmful intermediate gaseous compounds is eliminated or reduced.

10
11 Electro-chemical treatment of water containing nitrogenous contaminants has been
12 proposed (Lin & Wu, 1995 Jnl. Env. Sci. & Health, A30, 1445-1456). What is not
13 present in the prior art is the recognition that nitrogenous contaminants can be
14 transformed, by commercially practicable electrochemical processes, directly into
15 nitrogen gas, and thereby eliminated from the system.

16
17 In assessing whether a particular reaction will proceed electrolytically, the reaction
18 may be compared to the Nernst equilibrium equation:

19
$$E = E_0 - (RT/nF)\log_e(Q)$$

20 in which E is the cell voltage, E_0 is the cell voltage of a standard cell (calculated, or
21 derived from tables), Q is the concentration quotient, being the ratio of the
22 mathematical product of the concentrations of all the reaction products, divided by the
23 mathematical product of the concentrations of all the reactants. For example, at 25°C,
24 the term $(RT/nF)\log_e(Q)$ can be evaluated as $(0.0592/n)\log_{10}(Q)$.

25
26 One aspect of the present invention lies in determining, from an assessment of the
27 Nernst equation, whether electrolysis will be effective in a particular situation, to cause
28 contaminants to break down, and if so to what, and under what treatment conditions.

29
30 The Nernst relationships for many different transformations and conditions may be
31 plotted on a predominance field diagram, or phase diagram, or Pourbaix diagram, i.e
32 a nitrogen-oxygen-hydrogen Eh-pH solution phase diagram. Such a diagram is
33 published and available on a chemistry text book basis, as it relates to aqueous
34 nitrogenous compounds. Sets of the Nernst relationships appropriate to the

1 nitrogenous compounds are also available in table form, again on a text-book basis,
2 and that may also be used.

3
4 In carrying out a preferred form of the invention, the designer of the system may use
5 the Nernst relationships in a phase-diagram form, for example. The designer enters
6 on the phase diagram the Eh and pH that are measured in the contaminated system.
7 He then notes, from the diagram, the voltage V-Ngas at which, at the measured pH,
8 the predominating form of nitrogen is nitrogen gas. A computation is made as to the
9 voltage difference between V-Ngas and the voltage V-Eh as actually measured.

10
11 The designer then provides an electrochemical cell, having two electrodes (i.e an
12 anode and a cathode). If the nitrogenous contaminant is one (e.g dissolved nitrate)
13 which requires the addition of electrons in order to be transformed into gaseous
14 nitrogen, then it can pick up the electrons it needs from the cathode, and the designer
15 should arrange the cell so that the water flows by the cathode. The cell should be so
16 arranged as to its size, and the velocity of movement of water therethrough, that the
17 residence time of the water near the cathode is long enough for the transformation
18 reaction to be substantially completed.

19
20 Similarly, if the nitrogenous contaminant is one (e.g dissolved ammonium) which
21 requires the subtraction of electrons in order to be transformed into gaseous nitrogen,
22 then it can shed the excess electrons to the anode, and the designer should arrange
23 the cell so that the water flows by the anode. Again, the cell should be so arranged
24 as to its size, and the velocity of movement of water therethrough, that the residence
25 time of the water near the anode is long enough for the transformation reaction to be
26 substantially completed.

27
28 In either case, the engineer should set the voltage V-cell which will be applied
29 between the electrodes to a value at which the Eh voltage as measured in the vicinity
30 of one of the electrodes, after the electro-chemical reaction has been initiated, lies at
31 a voltage level, V-Ngas, at which nitrogen gas predominates. That is to say, the
32 engineer adjusts the electrical energy available at the electrodes to the effect that the
33 Eh voltage near one of the electrodes changes from V-Eh as measured initially to a
34 voltage that lies within the range of Eh voltages at which nitrogen gas predominates.

1
2 In either case, it may be noted, the other electrode basically serves no function in the
3 transformation reaction. (On the other hand, as will be explained later, sometimes
4 both the anode and the cathode of the same cell can be instrumental in releasing
5 gaseous nitrogen.)

6
7 It should be noted that in cases where very reductive conditions prevail, the Eh
8 voltage, V-Eh, as measured, may be negative.

9
10 As an example, in a particular case, a body of water contaminated with dissolved
11 ammonium may be identified as having an Eh voltage of, say, -0.53 volts. The pH of
12 the body may be measured at, say, 4.5. Given that the pH is not to be changed, the
13 designer traces up the diagram, at a constant pH, until he comes to an Eh voltage at
14 which the predominant phase of the nitrogen is nitrogen gas. It is found that nitrogen
15 gas predominates over a range of Eh voltages at that pH, i.e from about 0.0 volts to
16 about +0.3 volts. Given that range, the designer preferably should aim for an Eh
17 voltage of +0.15 volts.

18
19 (It is assumed that the pH of the water is a given, and that nothing is to be done to
20 change the pH. Sometimes, however, it is possible economically to change the pH,
21 and in that case such changes can be factored into the computations -- but it is a
22 benefit of the system as described herein that usually the pH may be left at whatever
23 value obtains naturally, and only the Eh voltage need be manipulated.)

24
25 In the exemplary case of water contaminated by ammonium at a pH of 4.5, the
26 designer should aim to set up the cell so that the Eh voltage of the water in the region
27 of the anode of the cell is about +0.15 volts. The engineer then adjusts the electro-
28 chemical parameters (including the voltage applied between the electrodes) in order
29 to produce the required Eh voltage V-Ngas near the anode -- being a voltage between
30 the limits V-Ngas-upper (0.3 volts) and V-Ngas-lower (0.0 volts). Preferably, the cell
31 is engineered to provide an Eh voltage in the vicinity of the anode of +0.15 volts.

32
33 To achieve this, the Eh voltage near the cathode might go even more negative, i.e
34 further away from promoting the gaseous phase of the nitrogen. But that does not

1 matter: when the water passes near the anode, nitrogen gas will bubble off, and when
2 the water passes the cathode, nitrogen gas will not bubble off. Only one of the
3 electrodes -- the anode in this case -- is effective.

4
5 Preferably, it should be arranged that the water moves through the cell (or cells) in
6 such a manner that all the contaminated water is caused to be close to the anode for
7 an adequate residence time.

8
9 It will be understood that when the contaminant is nitrate, the cathode now becomes
10 the electrode which is effective to transform the nitrogen into nitrogen gas. In an
11 exemplary case, the Eh might be measured at +1.1 volts, and the pH at 9.0. Now,
12 having carried out the Nernst calculations (or having inspected the phase diagram) the
13 engineer knows to arrange the electrochemical characteristics of the cell so that the
14 Eh voltage as measured in the vicinity of the cathode of the cell lies at about -0.1
15 volts, since that is a voltage at the middle of the range which, at a pH of 9.0, nitrogen
16 gas is the predominant phase.

17
18 The cathode and anode of the cell might be physically the same. In fact, the polarity
19 of the cell may be reversed periodically or cyclically. This can be useful for ensuring
20 that all the water gets treated, and also, switching the electrodes might serve to
21 prevent a build up of a coating on the anode, which sometimes is a problem.

22
23 In some cases, the Nernst equation indicates that the transformation to the nitrogen
24 gas phase can take place galvanically, i.e without the input of electrical energy from
25 an outside source, if the cell is engineered appropriately. In that case, the electrodes
26 would be of different materials, the anode being the material that is the more active in
27 the electro-chemical series.

28
29 It should be noted that the change of phase between the nitrogen gas phase and the
30 contaminant phase is gradual, not sudden. Thus, generally, the release of nitrogen,
31 although at a maximum at one particular Eh (for a given pH), still occurs, in most
32 cases, over quite a wide range of Eh. Of course, the expert knows that it is not
33 possible to measure Eh voltages of contaminated waters to a high degree of
34 consistency and accuracy, nor is it possible to set the cell voltage all that accurately.

1 It is recognised herein, however, that the margins of Eh voltage between which an
2 effective release of nitrogen gas will take place are wide enough that the inaccuracies
3 of measurement and adjustment, which are inevitable in practice, can be
4 accommodated.

5
6 The designer must see to it that sufficient electrical energy is available in the cell to
7 keep the Eh voltage in the contaminated water at the desired level, i.e between the
8 calculated /indicated limits. The resistance of the water should not be expected to
9 remain constant as treatment takes place, and in fact generally the resistance of the
10 cell may be expected to increase as the contaminant is eliminated. Thus, in order to
11 maintain the required Eh voltage in the water, more energy must be passed through
12 the cell. There may come a point, of course, at which it is no longer practical to
13 maintain voltage between the electrodes: but it is recognised herein that, in general,
14 waters that are contaminated with nitrogenous contaminants are of such a conductivity
15 that the required voltages at the electrodes can be maintained while supplying
16 electrical energy in an economical manner.

17
18 In many cases, it is economical to provide automatic control of the voltages, which
19 can be useful in a case where the Eh, pH, concentration of the contaminants, etc
20 might be subject to variation over a period of time.

21
22 It may be noted that carbonates, sulphates, chlorides, etc, and the like, may all be
23 present in addition to the nitrogenous contaminants in the water, and all these
24 substances can have an effect on the Eh voltage. However, it is recognised that the
25 single measurement of Eh takes care of all the substances. By contrast, it would be
26 difficult to determine what the Eh voltage should be, by calculation, taking account of
27 the various substances in their various concentrations. But, in most cases, a single
28 measure of the actual value of the Eh of the water is all that is needed: the voltage
29 that must be obtained to transform the nitrogen to nitrogen gas can also be easily
30 determined, e.g by inspection from the nitrogen phase diagram. This makes the
31 system easy to automate: even though the composition of the contaminants may
32 change, as the water passes by, and as a result of the treatment, all that need be
33 done to maintain efficiency is to periodically check the Eh and the pH, and adjust the
34 cell voltage accordingly.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

By way of further explanation of the invention, exemplary embodiments of the invention will now be described with reference to the accompanying drawings, in which:

Fig 1 is an Eh-pH diagram, which indicates the phases of nitrogen under the various conditions;

Fig 2 is a schematic diagram of a municipal sewage treatment installation, which embodies the invention;

Fig 3 is a cross-section of an area of contaminated ground around a well, undergoing electrolytic treatment;

Fig 4 is a section corresponding to Fig 3, showing galvanic treatment;

Fig 5 is a cross-section of an area of contaminated ground, undergoing electrolytic treatment;

Fig 6 is a plan view of an area of ground, undergoing treatment of the kind as shown in Fig 5.

The systems shown in the accompanying drawings and described below are examples which embody the invention. It should be noted that the scope of the invention is defined by the accompanying claims, and not necessarily by specific features of exemplary embodiments.

Fig 1 is an Eh-pH diagram for aqueous nitrogen species under the conditions stated. Whether the predominant form of the nitrogen in the water is ammonium, ammonia, nitrate, nitrite, or nitrogen gas, may be derived, according to the diagram, by entering the actual conditions of the variables, and reading off the redox voltages. Since it is desired that nitrogen gas be the predominant form, the engineer may read off the redox voltages, for a given pH, between which N_2 gas will predominate.

For example, at a pH of 7 the predominance field of nitrogen gas occurs between -250 mV (moderately reducing) and +150 mV (moderately oxidising) at a nitrogen activity of 0.8 atm, oxygen gas activity at 0.2 atm, and the activity of aqueous nitrogen

1 species fixed at 10^{-3} moles/litre.

2

3 (For the purposes of this specification, the term "activity" is used to indicate the ideal
4 thermodynamic concentration of a chemical species present in the system under
5 consideration. If the species is present as a gas, the activity may be measured as a
6 partial pressure; if the species is present as a non-volatile component, it may be
7 measured in terms of a concentration value, for example moles/litre.)

8

9 In applying the invention to the treatment of sewage water, an electrolytic/ galvanic
10 cell is set up, in which the sewage water is the electrolyte. The purpose of the cell is
11 to enhance the electrochemical oxidation of ammonium in the sewage water, and the
12 reduction of any residual or generated nitrate in the sewage water, both directly to
13 nitrogen gas, thereby minimising the escape of the toxic nitrogenous gases, and
14 allowing the preferential escape of non-toxic nitrogen gas.

15

16 Preferably, a bank of electrochemical cells is provided, each cell having anodic and
17 cathodic compartments connected by a salt bridge or an ion-selective membrane.

18

19 Fig 2 is an example of a water treatment plant. Raw sewage enters the primary
20 clarifier 20, where initial settling of solid material takes place. The water then passes
21 to a cell 23. The cell is divided by an ion-selective membrane 25, the two
22 compartments of the cell being given anode 27 and cathode 29 status by the action of
23 a voltage source 30.

24

25 Having passed through the anode 27, in which the ammonium in the sewage water is
26 oxidised and removed, the water passes to the aerobic tank 32, where BOD
27 (Biological Oxygen Demand) is reduced. (The tank 32 is of conventional design,
28 being, for example, a trickling tank, or an activated sludge tank.) Sludge is separated
29 and removed from the water in a settling tank 34. Biomass recycling takes place due
30 to the interaction of the tanks 32 and 34.

31

32 Water from the settling tank 34, which contains nitrate, passes to the cathode
33 compartment 29 of the cell 23, where the nitrate is broken down and removed. As
34 shown, the water from the settling tank 34 may first be passed through one or more

1 powered cells 36, which serve to ensure that the breakdown and removal of all the
2 ammonium and nitrate is as complete as possible.

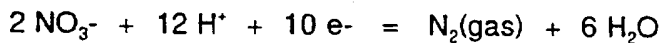
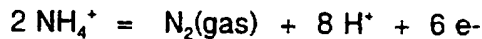
3
4 The clean effluent water can be further treated with chlorine, as at 38, if desired.

5
6 The electrons released in the anodic compartment 27 by the oxidation of the
7 ammonium are collected by the anode, and pass via external wiring to the cathode
8 29, there to promote the reduction of residual nitrate to N₂ gas. (If nitrate is absent,
9 under anaerobic conditions hydrogen (H⁺) will probably serve as the electron acceptor,
10 only minor oxygen being present under the existing redox conditions.)

11
12 Each cell operates independently of the others and can be isolated when maintenance
13 is required.

14
15 So long as the redox voltage is maintained within the indicated limits (Fig 1) only a
16 single-stage treatment system is required. This treatment cell is arranged to control
17 the redox potential of the solution within the predominance field of nitrogen gas.

18
19 Two reactions of interest are:

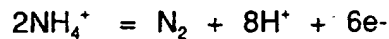


24
25 Nitrogen gas is the most stable phase under typical earth surface conditions (pH 3-10,
26 redox potential -0.5 to +1.2 volts), so the conversion to gas is nearly always
27 thermodynamically favoured. It is recognised herein that, with the nitrogenous
28 contaminants, the conditions needed to transform the contaminant to nitrogen gas are
29 within comparatively easy reach, from which it is recognised that the size of the facility
30 needed to treat the water, residence times, etc, can be engineered on an economical
31 scale.

32
33 As to their physical structure, the electrodes of the cell 23 may be of porous graphite,
34 iron, magnetite, etc. The set-up generally requires separate anodic and cathodic

1 compartments, connected via an ion-selective membrane.

2
3 The anodic reactions may be described as follows. More than 90% of the nitrogen in
4 sewage water is present as ammonium (NH_4^+), and it is the aim to oxidise the
5 ammonium directly to nitrogen gas. The reaction to be encouraged is:



7 The standard cell voltage, E_0 in the Nernst equation, typically would be -0.28 V.

8
9 The electrolytic cell is used to provide the electrical energy required to initiate this
10 otherwise unfavourable chemical reaction.

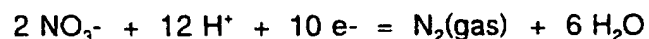
11
12 The Nernst equation is utilized to evaluate the optimal extent of the electrolytic
13 conversion. The Nernst relationship shows how redox potential of the half-cell
14 changes with concentrations of reactants and products:

$$15 \quad E = -0.28\text{V} + 0.0788 \text{ pH} - 0.0098 \log \text{PN}_2 + 0.0197 \log \text{NH}_4^+$$

16 from which it can be seen that E (voltage) becomes more positive by (a) maximising
17 the pH, (b) maximising the NH_4^+ , and (c) minimising the $p(\text{N}_2)$ by withdrawing the
18 nitrogen gas as it is produced.

19
20 However, the small coefficients on the various terms in the Nernst equation indicate
21 that the potential should be affected only very slightly by changes in the pH and
22 ammonium content of the influent solution, and by the pressure of nitrogen (in
23 practice, fixed to a value near the atmospheric level of 0.78 atm).

24
25 The nitrate is broken down in the cathode compartment 29. The cathodic reactions
26 may be described as follows. The intended cathodic reaction is:



28 The standard cell voltage, E_0 , would be 1.24 V, whereby this is a spontaneous
29 reaction. The reactions that result in the formation of N_2O and NO are also
30 spontaneous; however, by controlling the voltage within the field of predominance of
31 N_2 gas, as described, the formation of the nitrous and nitric oxide species may be
32 inhibited.

33
34 The Nernst relationship for the above equation is:

$$E = 1.24 \text{ V} - 0.0709 \text{ pH} - 0.0059 \log \text{PN}_2 + 0.0118 \log \text{NO}_3^-$$

2

3 It is an aim of the system as described that ammonia /ammonium in sewage water
4 may be broken down, by electrolysis, directly into nitrogen gas. This is contrasted
5 with the conventional biochemical reaction, which has many intermediate stages that
6 can lead to the release of toxic gases.

7

8 The invention may be applied in applications other than municipal-scale sewage
9 treatment, as will now be described.

10

11 The invention may be used to treat groundwater contaminated with nitrate. The
12 cathodic reaction is as described previously; but the anodic reaction will probably
13 involve the oxidation of water, as follows:



15

16 Generally, treatment of groundwater contaminated with nitrate has been considered
17 very expensive. It is recognised that major cost benefits arise from carrying out
18 electrolysis on groundwater in-situ, as compared with electrolysis treatment systems
19 which involve passing the water to be treated through an engineered treatment facility.
20 Such systems involve the expense of the provision of a means for routing the water to
21 be treated out of the ground, and into and through the facility, and because the facility
22 itself has to be physically large to contain the volumes of water that need to be
23 treated.

24

25 In-situ electrolytic treatment of groundwater incurs reduced expense, especially as to
26 capital cost, because the treatment is carried out with the water remaining in the
27 ground, and therefore the cost of engineering a treatment facility, and of engineering a
28 means for moving the water into and out of the facility, is avoided or reduced.

.29

Fig 3 shows a drinking-water well 40, having a metal (steel) casing 43. Nitrate, e.g. from agricultural run-off, is contaminating the local groundwater, to the extent of polluting the water drawn up from the well. Carbon rods 45 are inserted into the ground in such a way as to make contact with the nitrate-contaminated water. A voltage source 47 is connected as shown, so as to turn the well-casing 43 into a

1 cathode and the rods 45 into an anode.

2
3 The influence of the cathode at the well extends several meters into the surrounding
4 ground, and of course is strongest close to the well. As described, the cathodic
5 reaction serves to reduce or eliminate the nitrate from the water.

6
7 Sometimes, even a galvanic cell (i.e a cell having no source of electrical energy) can
8 create a sufficiently vigorous reduction of the nitrate that the nitrate is treated
9 effectively. Fig 4 shows the anode 49 in such a case. The anode is of an electro-
10 active metal, such as magnesium.

11
12 Fig 5 shows a case where nitrate-laden water is to be treated, not at a well as in Figs
13 3 and 4, but while passing through the ground. Two carbon rods 50,52 and a voltage
14 source 54 are so placed that the cathode 50 lies within the area of contaminated
15 groundwater, and the anode 52 lies in the groundwater outside the contaminated
16 area. (The demarcations between contaminated and uncontaminated of course are
17 characterised by gradual, not sharp, changes in concentration of the contaminant.)

18
19 As shown in Fig 5, sensors 56 are provided for monitoring the pH and Eh of the
20 groundwater. Signals from these sensors are processed by a computer 58, and the
21 result fed to the voltage source 54. Thus, if the Eh (or indeed the pH) of the water
22 should change, the voltage is adjusted. Similarly, a check can be kept that the right
23 amount of electrical energy is being supplied to keep the voltage at the desired level.
24 The "before" and "after" measurements can be compared, for checking the efficacy of
25 the treatment system.

26
27 Sometimes, only one cell is needed. If more than one is needed, the extra cells are
28 added in the same manner, ie with the cathode inside the contaminated area and the
29 anode outside. Fig 6 shows a plan of a typical area of ground in which the
30 groundwater is contaminated with nitrate. Two cells are shown, and other cells may
31 be added later, as the contaminated zone moves, or to give more efficacy to the
32 treatment.

33
34 In Fig 6, two cells are provided. The required voltage is supplied between the

1 cathode 60 and the anode 62 of the first cell 63. The cathode 60 creates an area of
2 influence 64, in which the nitrate is transformed into nitrogen gas. The anode has
3 substantially no effect on the contaminant. The second cell 67 is similar.
4

5 In Fig 6, as shown, the reason treatment is being undertaken is because drinking-
6 water wells 68 are located in the path of the oncoming plume of nitrate. These wells
7 may be further protected from any nitrate that escaped the cells 63,67. The protection
8 is the same as shown in Fig 3.
9

10 When more cells are added, these can be added as electrically-separate units, or they
11 may be connected in series, or in parallel, with the existing cells. The engineer
12 should make sure the voltage at the electrodes are maintained, and the manner of
13 connection is secondary to that.
14

15 The invention is intended for use generally in setting up large scale electrolysis cells,
16 preferably in-situ, with or without added electrical energy. Electrodes may be
17 engineered to be suitable for the needs of the individual case.
18

19 The engineer should take account of the effects of electrochemical activity at the
20 anode (in both the electrolytic and the galvanic cases) in that electrolysis of the water
21 at the anode will lead to the generation of hydrogen ions, and an increase in acidity.
22

23 If the water is naturally alkaline, a little extra acidity would not matter. However, if the
24 water is naturally acidic, further acidity might be a problem. If so, the engineer might
25 decide to provide the anode in a sacrificial material, whereby acidity generated at the
26 anode would be reduced.
27

28 Since the material of the sacrificial anode passes into the water, the material should
29 be selected on the basis of being environmentally friendly in water. Magnesium, for
30 example, has very low toxicity in water, and is a good choice for the sacrificial anode.
31 Aluminum, on the other hand, can be toxic in water, and is contra-indicated. In some
32 cases, for example if the water contains such potentially toxic materials as dissolved
33 aluminum and other metals, the preferred sacrificial anodic material would be iron,
34 because iron can promote co-precipitation of dissolved metals.

1 Other areas of applicability for the technology are:

2 - Treatment of well water. Many wells are contaminated with nitrate. The electrolytic
3 cell in the well converts nitrate to nitrogen gas.

4 - Treatment of an aquifer contaminated with nitrate, at depth (where there is little
5 biological activity to reduce the nitrate). The electrolytic cell arises by placing
6 electrodes in the aquifer. Electrolysis reduces the nitrate to nitrogen gas.

7 - Treatment of animal waste collection tanks. Here, the waste material is, for
8 example, in a tank under a pig barn. In addition to addressing the ammonium, as
9 described, electrolysis converts hydrogen sulphide to H^+ and SO_4^- and converts
10 methane to H^+ and CO_2 .

11 - Treatment of mine waste water. Ammonium nitrate + diesel fuel, as used for
12 explosives, leaves ammonia (NH_3) dissolved in the water. Electrolysis converts the
13 ammonia to nitrogen gas.

14 - Treatment of waste water from the food processing industry (e.g pickling plants).

15
16 Other points to be considered in relation to the treatment of contaminated water by
17 electrolysis as described herein are:

18 - The efficacy of the electrolysis reaction is generally much less dependent on
19 temperature than biochemical reactions. Biological denitrification at $10^\circ C$ may be
20 expected to be an order of magnitude less than at $25^\circ C$. The electrolysis reaction can
21 be expected to take place efficiently even in prolonged freezing weather.

22 - The conventional biological treatment produces sludge. The electrolysis reaction
23 can be expected to produce a comparatively smaller amount of sludge.

24 - Electrolysis circumvents the need to add a carbon source, which is needed in
25 conventional biological denitrification for maintaining reaction rate and completion.

26 This may also reduce the volume of sludge produced.

27 - Biochemical reactions typically proceed slowly, whereby long residence times are
28 required for treatment to be completed. The electrolysis reactions can be expected to
29 be completed in shorter periods, thus avoiding the long residence times.

30 - If an electrolysis system is found to be inadequate, often the inadequacy can be
31 remedied simply by adding a further electrolytic treatment facility, in series with the
32 already-present facility. The expense of doing that is hardly more than the expense of
33 providing the larger system originally would have been. By contrast, if a biological
34 system is found to be inadequate, generally it cannot be remedied in that way, i.e

1 simply by adding another small system. Rather, what is required is that the
2 inadequate biochemical system must be removed, and a whole larger system installed
3 in its place. Therefore, the prudent designer of a conventional biochemical system
4 had to take care to make a contingency provision, at the time the system was
5 installed, often at considerable expense, for future increased demands on the system.
6 The designer of the electrolytic system, on the other hand, can engineer the system
7 just for today's needs, knowing that the system can easily be upgraded later if the
8 need should arise.

9
10 The term Eh as used herein is defined as follows. The Eh voltage of a solution is the
11 redox potential generated in the solution by comparison with a standard hydrogen
12 electrode. A standard hydrogen electrode comprises a platinum wire with hydrogen
13 bubbling around it, contained within a solution of hydrogen ions in solution of 10^0
14 moles per litre (the zero pH condition).

Claims

1 **CLAIM 1.** Procedure for treating water contaminated by a nitrogenous contaminant,
2 comprising the step of providing an electrochemical cell in the contaminated water,
3 and of engineering an electrochemical reaction in the contaminated water, which is
4 effective to change the Eh voltage of the water to a voltage at which the
5 contaminant transforms into gaseous nitrogen.

1 **CLAIM 2.** Procedure of claim 1, including the steps of:
2 measuring the pH of the nitrogen-contaminated water;
3 determining, for that pH as measured, the voltages V-Ngas-upper and V-Ngas-lower,
4 being the limiting Eh voltages between which the predominant nitrogen phase is
5 nitrogen gas;
6 providing a pair of electrodes in the water, the electrodes being in electrolytic
7 communication with each other through the contaminated water, thereby creating
8 an electrochemical cell in the water, the contaminated water comprising the
9 electrolyte of the cell;
10 providing a voltage V-cell between the electrodes;
11 measuring the Eh voltage V-Eh of the water;
12 and controlling the voltage V-cell to such a value as to maintain an Eh voltage in the
13 water in the vicinity of one of the electrodes at a voltage V-Ngas, being an Eh
14 voltage between V-Ngas-upper and V-Ngas-lower.

1 **CLAIM 3.** Procedure of claim 2, including the step of maintaining the Eh voltage of the
2 contaminated water substantially halfway between the said voltages V-Ngas-upper
3 and V-Ngas-lower.

1 **CLAIM 4.** Procedure of claim 1 including the step of applying and maintaining
2 electrical energy from an outside source between the pair of electrodes, of such
3 magnitude as to maintain the said voltage V-cell between the electrodes.

1 **CLAIM 5.** Procedure of claim 2 including the step of providing a nitrogen-oxygen-
2 hydrogen Eh-pH solution phase diagram, and of using same to determine the
3 V-Ngas-upper and V-Ngas-lower voltage levels.

1 **CLAIM 6.** Procedure of claim 2 including the step of so arranging the cell that the
2 contaminated water comprising the electrolyte of the cell is water that is moving or
3 flowing relative to the electrodes.

1 **CLAIM 7.** Procedure of claim 6, including the steps of establishing the presence of a
2 body of the contaminated water, of providing a plurality of the cells in the body of
3 contaminated water, and of so arranging the cells that the contaminated water
4 flows from cell to cell.

1 **CLAIM 8.** Procedure of claim 2, wherein, in a case where a desired V-Ngas voltage is
2 determined to be lower than V-Eh, whereby electrons need to be added to the
3 contaminant to transform the nitrogen in the contaminant to the gaseous nitrogen
4 phase, the procedure includes the step of ensuring the flowing water passes close
5 to the cathode.

1 **CLAIM 9.** Procedure of claim 8, wherein the contaminant is nitrate.

1 **CLAIM 10.** Procedure of claim 2, wherein, in a case where a desired V-Ngas voltage
2 is determined to be greater than V-Eh, whereby electrons need to be removed from
3 the contaminant to transform the nitrogen in the contaminant to the gaseous phase,
4 the procedure includes the step of ensuring the flowing water passes close to the
5 anode.

1 **CLAIM 11.** Procedure of claim 10, wherein the contaminant is ammonium.

1 **CLAIM 12.** Procedure of claim 2, including the step of ensuring a sufficient size of the
2 cell and the electrodes, and of ensuring a sufficient residence time of the water
3 close to the electrodes, as to ensure effective transformation of the nitrogenous
4 contaminant to nitrogen gas.

1 **CLAIM 13.** Procedure of claim 2, wherein the procedure includes the steps of:
2 providing a first cell, in which a desired V-Ngas voltage is determined to be greater
3 than V-Eh, whereby electrons need to be removed from a first contaminant to

4 transform the nitrogen in the contaminant to gaseous nitrogen;
5 providing a second cell, in which a desired V-Ngas voltage is determined to be lower
6 than V-Eh, whereby electrons need to be added to a second contaminant to
7 transform the nitrogen in the contaminant to gaseous nitrogen;
8 providing the first and second cells in a contiguous configuration, the two cells being
9 separated by an ion-selective membrane;
10 whereby at least some of the electrons produced by the first cell are supplied to the
11 second cell.

1 **CLAIM 14.** Procedure of claim 2, wherein the contaminated water is groundwater in
2 an aquifer, and the procedure is carried out on the groundwater in-situ.

1 **CLAIM 15.** Procedure of claim 14, wherein the contaminant is nitrate, and wherein the
2 cathode of the cell is a metal casing of a well, and wherein the procedure includes
3 the step of providing the anode in the form of a conductive rod inserted in the
4 material of the aquifer, adjacent to the well.

1 **CLAIM 16.** Procedure of claim 2, wherein the contaminant is dissolved excrement of
2 farm animals, and the water is contained in a vessel.

1 **CLAIM 17.** Procedure of claim 2, wherein the contaminant is municipal sewage, and
2 the water is contained in a vessel.

1 **CLAIM 18.** Procedure of claim 2, including the steps of providing a voltage control
2 means, which is effective to increase or decrease the electrical energy supplied to
3 the electrodes, for maintaining the voltage V-cell between the electrodes at the said
4 level.

1 **CLAIM 19.** Procedure of claim 18, wherein the procedure includes the steps of:
2 monitoring the pH and Eh of the contaminated water, and computing a consequently-
3 required level of the voltage V-Ngas, on an on-going basis;
4 providing a voltage control means, which is responsive to the said consequently-

5 required level of the voltage V_{Ngas} , and is effective to increase or decrease the
6 electrical energy supplied to the electrodes, for maintaining the voltage V_{cell} between
7 the electrodes at the consequently-required level.

1 CLAIM 20. Procedure of claim 1, wherein the procedure includes the steps of:
2 measuring the pH of the nitrogen-contaminated water;
3 determining the nature of, and concentration of, the nitrogenous contaminant, and of
4 ascertaining the desired stoichiometric parameters of a reaction for transforming
5 the contaminant into gaseous nitrogen;
6 by use of the Nernst equation, determining a level V_{Ngas} of the Eh voltage that will
7 produce a transformation of the contaminant into gaseous nitrogen by that
8 reaction;
9 providing a pair of electrodes in the water, the electrodes being in electrolytic
10 communication with each other through the contaminated water, thereby creating
11 an electrochemical cell in the water, the contaminated water comprising the
12 electrolyte of the cell;
13 measuring the Eh voltage V_{Eh} of the water;
14 and controlling the voltage V_{cell} to such a value as to maintain an Eh voltage in the
15 water in the vicinity of one of the electrodes at the voltage V_{Ngas} .

1 CLAIM 21. Procedure of claim 2, wherein the material of the anode is sacrificial, in
2 that the material of the anode is of the kind that passes into solution in the water as
3 a result of electrochemical activity.

1 CLAIM 22. Procedure of claim 21, wherein the contaminated water is acidic.

1 CLAIM 23. Procedure of claim 21, wherein the material of the anode is, or includes,
2 magnesium.

1 CLAIM 24. Procedure of claim 21, wherein the contaminated water contains a
2 potentially toxic dissolved metal, and the material of the anode is, or includes, iron.

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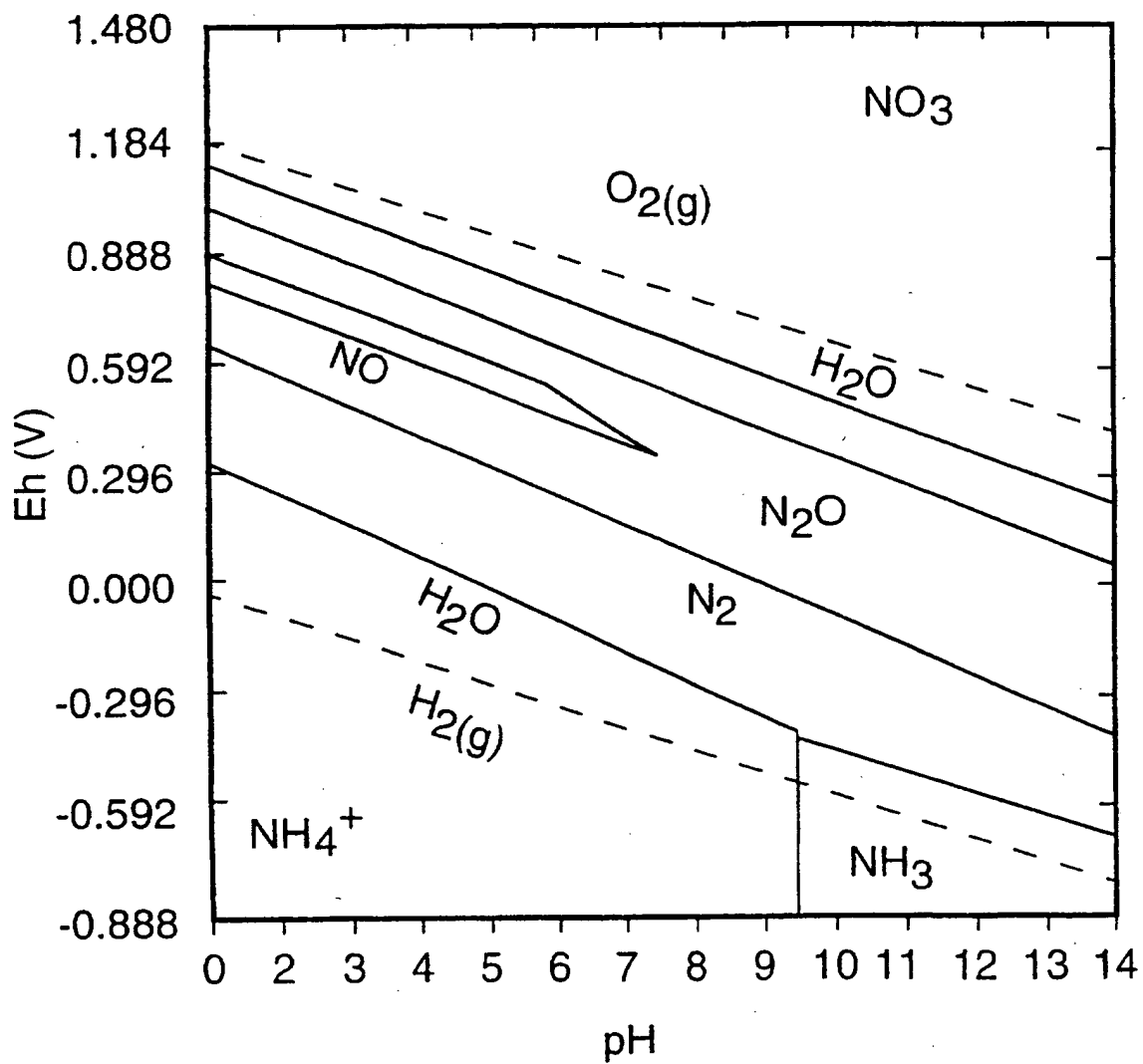


FIG.1

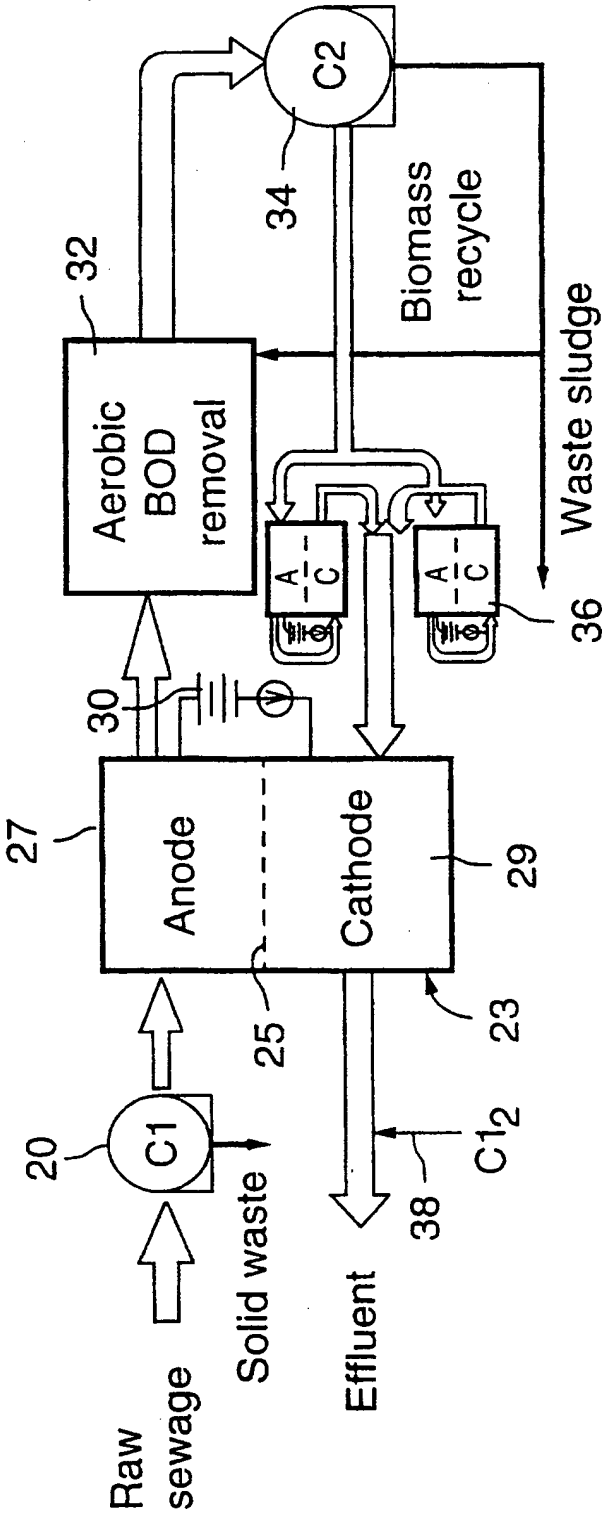


FIG.2

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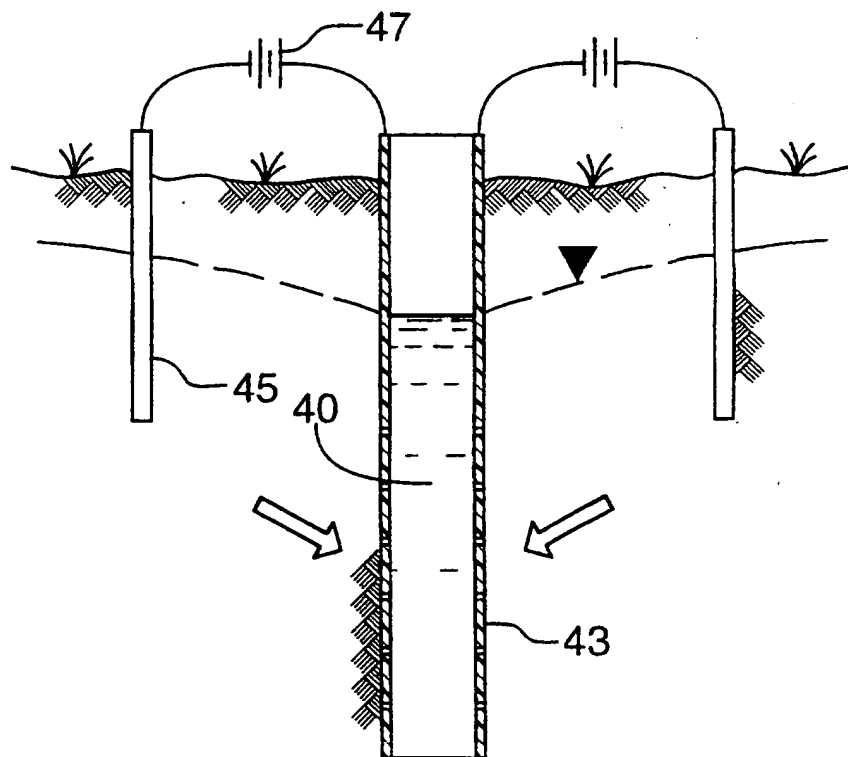


FIG.3

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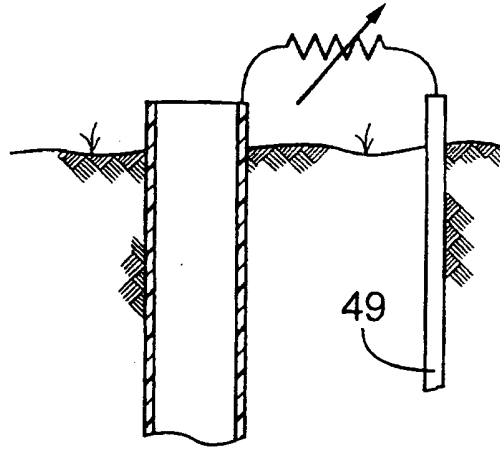


FIG. 4

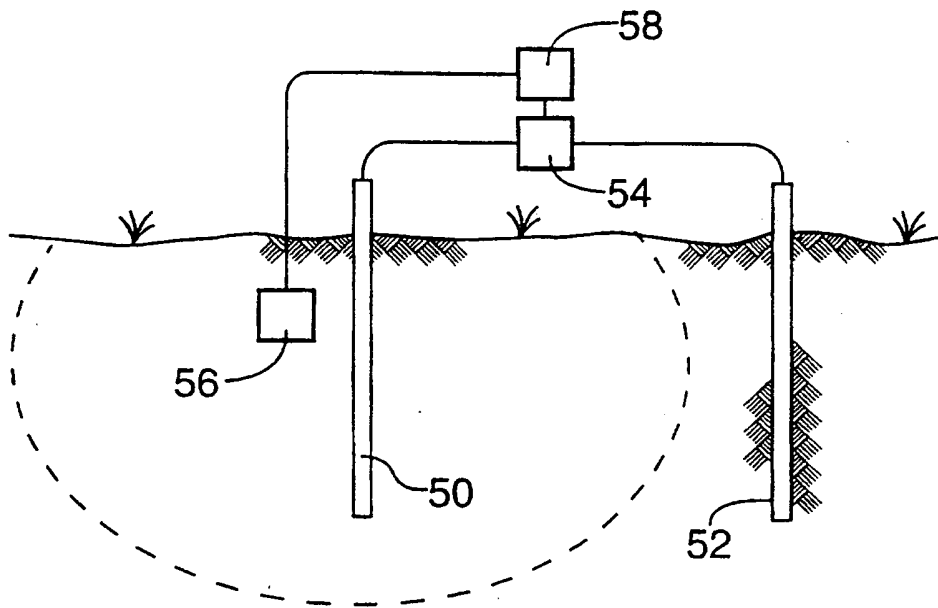


FIG. 5

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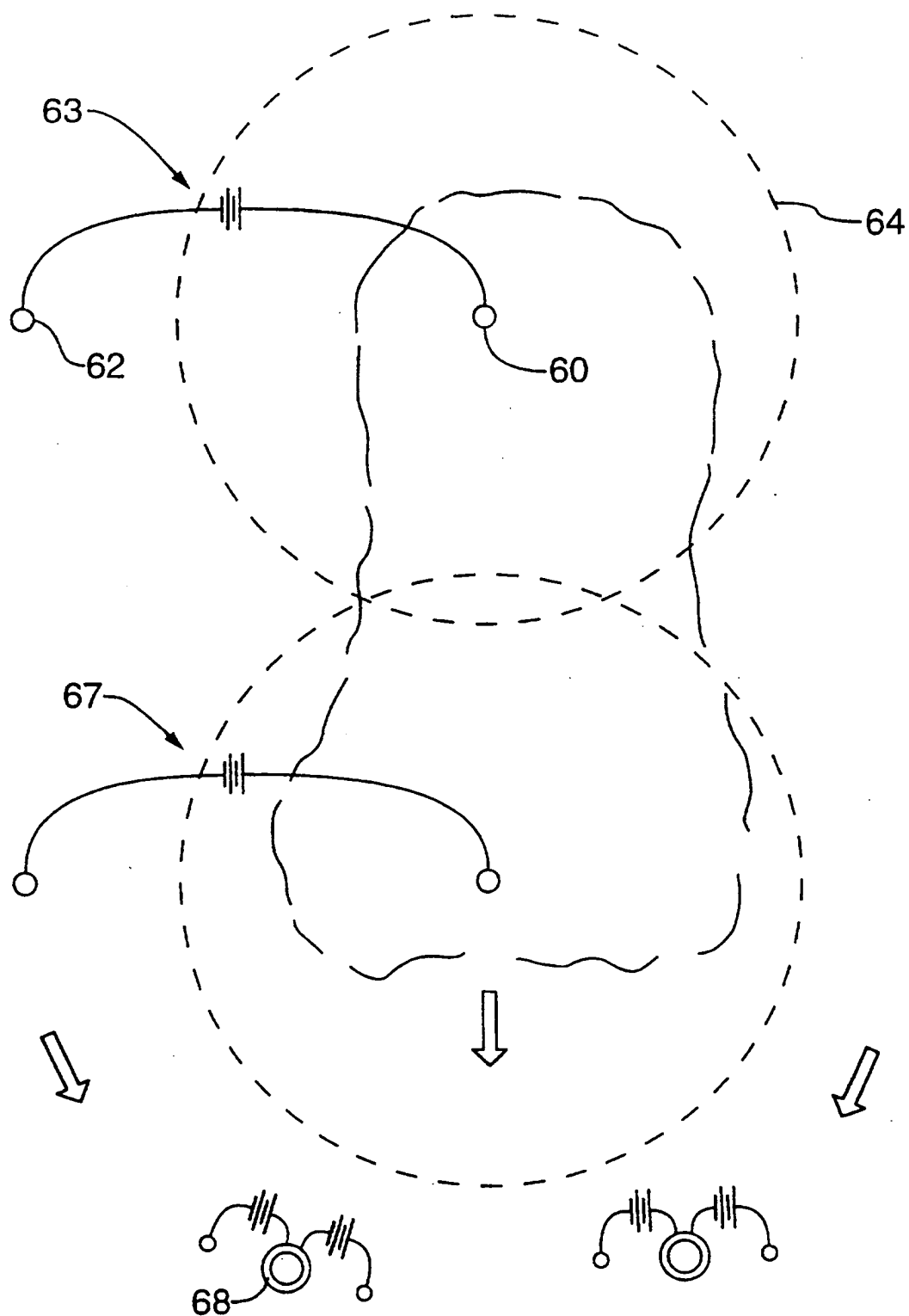


FIG.6

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 97/00122

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C02F1/46 C02F1/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C02F B09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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X A	EP 0 659 692 A (HAHNEWALD GMBH) 28 June 1995 see the whole document ---	1 2,8,9,20
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

27 May 1997

Date of mailing of the international search report

06.06.97

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INTERNATIONAL SEARCH REPORT

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